

LC/MS/MS Analysis for Restricted Chemicals in Textiles

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Overview

- The methods were developed for analyzing the different class of restricted chemicals in textiles, especially for aromatic amines and azo dyes.
- The co-injection method using pretreatment program with the autosampler (SIL-30AC) in the aromatic amines analysis allowed more efficient analysis omitting the manual operation.
- For azo dyes analysis, dilution of samples can reduce the matrix effect contributed by the interference from the textile samples.

1. Introduction

In recent years, the safety concern over textiles has been on the rise in addition to the environmental and food safety issues. Harmful substances in textiles are being regulated around the world, particularly the EU region. Besides the regional regulations, there are also strict regulations to ensure the safety of consumers. These include the adoption of independent inspection and certification on residual standard references such as STANDARD 100 by OEKO-TEX® and chemical regulatory lists implemented by the manufacturer. Hence, we have developed the LC/MS/MS method package for textiles which include aromatic amines, azo dyes, perfluoro compounds, alkylphenol ethoxylates, and alkylphenols. Here, we introduce the results of the analyses of aromatic amines and azo dyes and how to effectively use the method package.

2. Methods

2-1: Aromatic Amine

A Shimadzu LCMS-8045 triple quadrupole LC/MS/MS system was used to develop the MRM method for quantitative analysis of 24 aromatic amines. A Shim-pack FC ODS column (150 x 2.0 mm) was used for the separation using a 13 minutes' gradient elution program. The analytical conditions are as shown in Table 1. The sample preparation is conducted according to ISO 14362. The final extracted sample was in a pure organic solvent. Due to the nature of the diluent, it is insufficient to be retained on the ODS column. Hence, there is a need to modify the diluent. In this experiment, autosampler SIL-30AC has the pretreatment program function, which can co-inject the sample with water, improving the retention of the analytes. This function makes it possible to omit the manual dilution operation. (See Figure 1)

LC conditions (Nexera X2)	MS conditions (LCMS-8045)
Column : Shim-pack FC ODS (150 mmL x 2.0 mm I.D., 3 μm)	Ionization : ESI (Positive)
Mobile phase A : Water with 5mM Ammonium Acetate (pH3.0)	Nebulizing gas flow : 3.0 L / min
Mobile phase B : Acetonitrile	Drying gas flow : 5.0 L / min
Time program : 2%B (0.0mins to 1.00 mins) → 100%B (6.00 min to 9.00 min) → 35%B (9.01 min to 13.00 min)	Heating gas flow : 15.0 L / min
Flow rate : 0.3 mL / min	Interface temperature : 400°C
Column temp. : 40°C	DL Temperature : 300°C
Injection volume : 5 μL	Block Temperature : 500°C

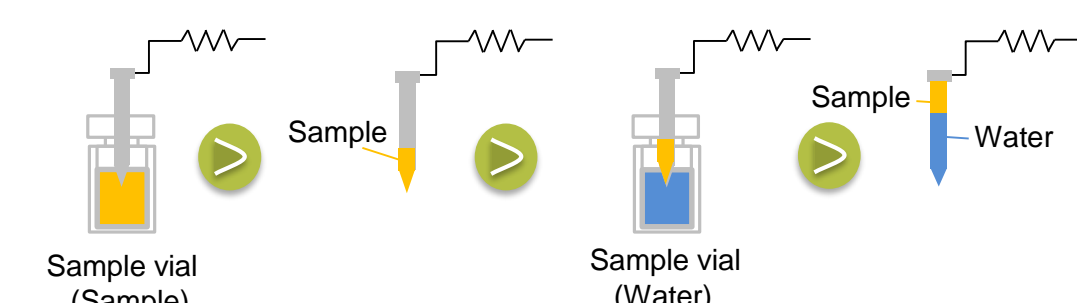


Figure 1 Pre Treatment Function (SIL-30AC)

2-2: Azo dyes-Method 1

Not all azo dyes could be analyzed steadily with a single LC/MS/MS method due to their chemical properties. Hence, it was divided into two (for 44 and 7 compounds). A Shimadzu LCMS-8045 triple quadrupole LC/MS/MS system was also used to develop the MRM method for quantitative analysis of 44 aromatic amines. A Shim-pack FC ODS column (75 x 2.0 mm) was used for the separation using a 20 minutes' gradient elution program. The analytical conditions are as shown in Table 2. In this study, a simple extraction method was employed via ultrasonication at elevated temperature for textile sample (cotton based) (Figure 2). The extracts spiked standard samples (final concentration: 10 ng/mL) were applied to examine the matrix effect.

LC conditions (Nexera X2)	MS conditions (LCMS-8045)
Column : Shim-pack FC ODS (75 mmL x 2.0 mm I.D., 3 μm)	Ionization : ESI (Positive/Negative)
Mobile phase A : Water with 5mM Ammonium Acetate	Nebulizing gas flow : 2.0 L / min
Mobile phase B : Acetonitrile:Water (9:1) with 5mM Ammonium Acetate	Drying gas flow : 10.0 L / min
Time program : 35%B (0.0mins to 0.50 mins) → 100%B (12.00 min to 17.00min) → 35%B (17.01min to 20.00min)	Heating gas flow : 10.0 L / min
Flow rate : 0.3 mL / min	Interface temperature : 300 °C
Column temp. : 40°C	DL Temperature : 250 °C
Injection volume : 5 μL	Block Temperature : 400°C

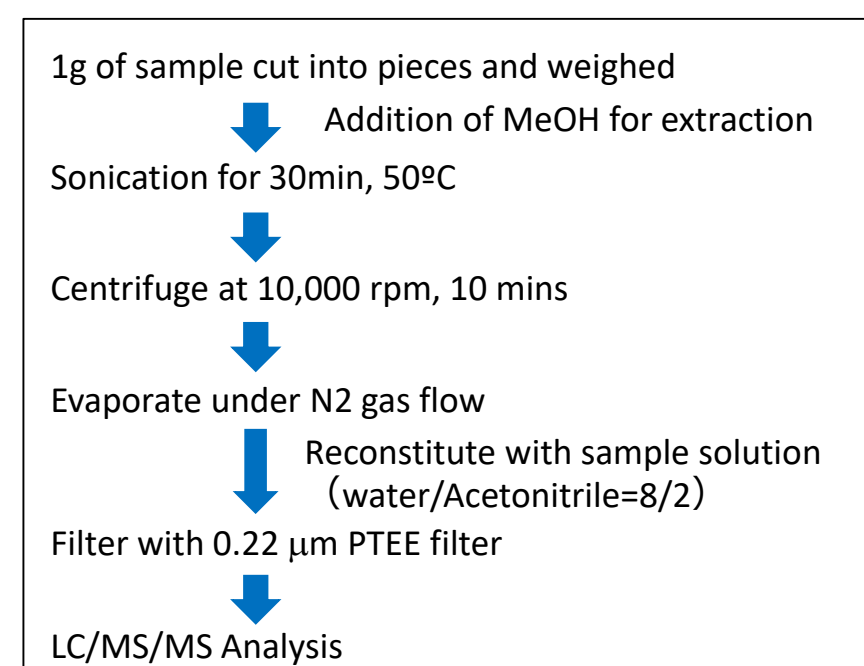


Figure 2 Preparation Protocol

2-3: Azo dyes-Method 2

A Shimadzu LCMS-8045 triple quadrupole LC/MS/MS system was also used to develop the MRM method for quantitative analysis of 7 azo dyes which could not be analyzed steadily with Method 1. A Shim-pack FC ODS column (75 x 2.0 mm) was used for the separation using a 10 minutes' gradient elution program. The analytical conditions are as shown in Table 3. The sample preparation procedure is similar to azo dye method 1. In this study, the extracts spiked samples (final concentration: 50 ng/mL) were applied to examine the matrix effect.

LC conditions (Nexera X2)	MS conditions (LCMS-8045)
Column : Shim-pack FC ODS (75 mmL x 2.0 mm I.D., 3 μm)	Ionization : ESI (Positive/Negative)
Mobile phase A : Water with 5mM Ammonium bicarbonate	Nebulizing gas flow : 2.0 L / min
Mobile phase B : Acetonitrile	Drying gas flow : 10.0 L / min
Time program : 2%B (0.0mins to 0.50 mins) → 90%B (6.00 min to 7.50min) → 2%B (7.51min to 10.00min)	Heating gas flow : 10.0 L / min
Flow rate : 0.3 mL / min	Interface temperature : 300 °C
Column temp. : 40 °C	DL Temperature : 250 °C
Injection volume : 5 μL	Block Temperature : 400 °C

3. Results

3-1: Aromatic Amines

The results of these analyses with LCMS-8045 provided good linearities ($R^2 > 0.99$) and wide dynamic ranges (See Table 4). Using the method developed for the method package, detection limit of aromatic amines are below the regulation values of 20mg/kg (20ppm). MRM chromatograms (See Figure 3) showed both using the manual dilution method and using the automated pretreatment program. These chromatograms showed that all 24 aromatic amines provide similar results and retention time. Thus, suggesting the reliability of the automated pretreatment program of the autosampler.

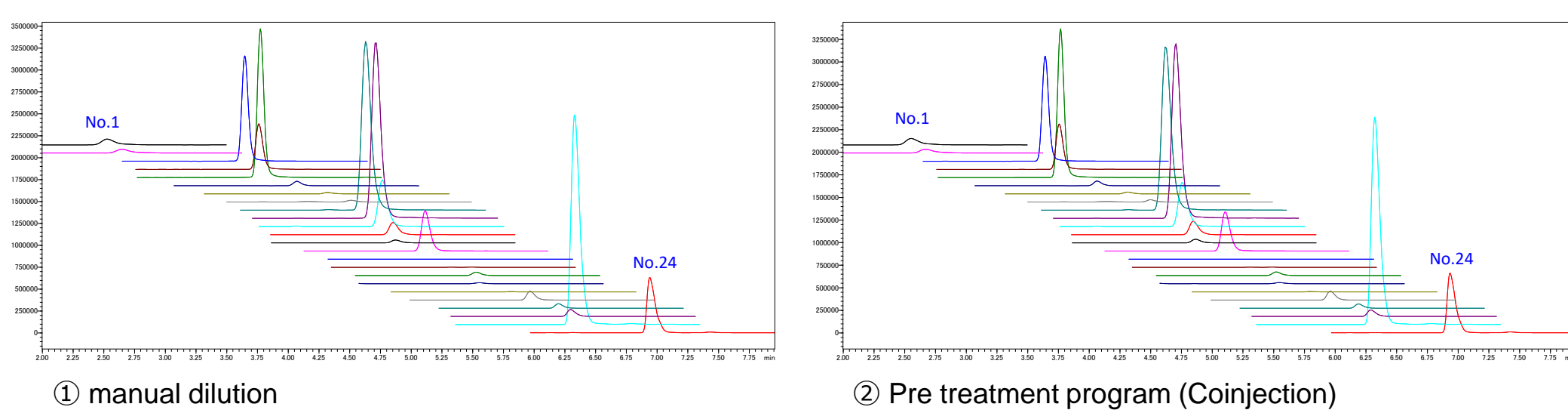


Figure 3 MRM chromatograms of 24 aromatic amines (100ng/mL) with (1) manual dilution and (2) automated dilution

Table 4 Quantitation results for 24 aromatic amines

No	Compound Name	RT (min)	Linearity	Range (ng/mL)
1	2,4-Diaminoazole	2.502	0.9973	2-1000
2	2,4-toluenediamine	2.627	0.9997	2-500
3	4,4'-oxydianiline	3.649	0.9995	1-200
4	Benidine	3.758	0.999	1-100
5	4,4'-diaminodiphenylmethane	3.769	0.9999	0.2-200
6	o-Anisidine	4.068	0.9998	2-1000
7	o-toluidine	4.315	0.9998	5-1000
8	2,6-Xyldine	4.498	0.9994	5-1000
9	4,4'-methylene-o-toluidine	4.609	0.9994	0.2-500
10	3,3'-dimethoxybenzidine	4.707	0.9997	1-200
11	o-Tolidine	4.758	0.9987	1-100
12	p-Cresidine	4.85	0.9992	2-1000
13	2,4,5-Trimethylalanine	4.856	0.9997	5-500
14	4,4'-thiodianiline	5.121	0.9996	0.5-1000
15	4-Chloroaniline	5.32	0.9999	100-1000
16	5-Nitro-o-toluidine	5.344	0.9984	100-1000
17	2,4-Xyldine	5.567	0.9989	50-1000
18	2-Naphthylamine	5.543	0.9997	5-1000
19	4-Chloro-o-toluidine	5.833	0.9977	10-1000
20	4-Aminobiphenyl	5.986	0.9993	2-500
21	3,3'-dichlorobenzidine	6.22	0.9996	5-100
22	4,4'-methylene-bis-2-chloroaniline	6.316	0.999	0.5-100
23	4-aminoazobenzene	6.353	0.9987	0.5-100
24	o-Aminoazotoluene	6.963	0.9992	0.1-100

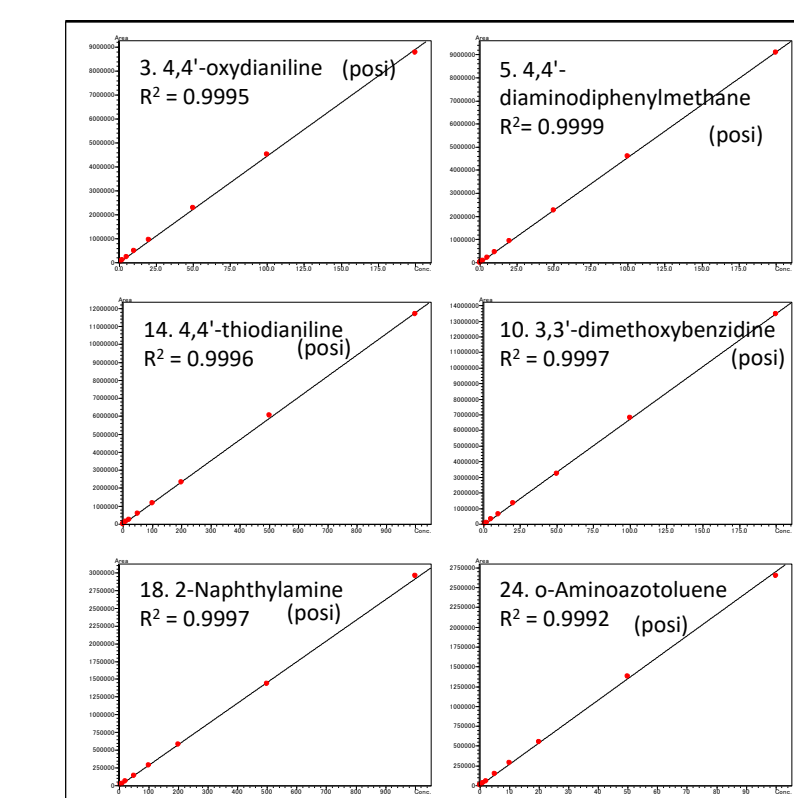


Figure 4 Calibration curves for aromatic amines

3-2: Azo dyes-Method 1

The results of 44 azo dyes with LCMS-8045 provided good linearities ($R^2 > 0.99$) and wide dynamic ranges (See Table 5). Using the method developed for the method package, detection limit for the 44 azo dyes are way below the regulation values of 50mg/kg (50ppm). Matrix effect for azo dyes in textile samples are found to be within the range of 33.1% ~ 168.7%. It can be significantly improved with further dilution to the sample solution, giving a new range of 66.5% ~ 108.7%. For example, disperse red 1 displayed a severe matrix effect of 33.1%. However, with the help of the dilution of the sample, the matrix effect significantly improved to 90.1%.

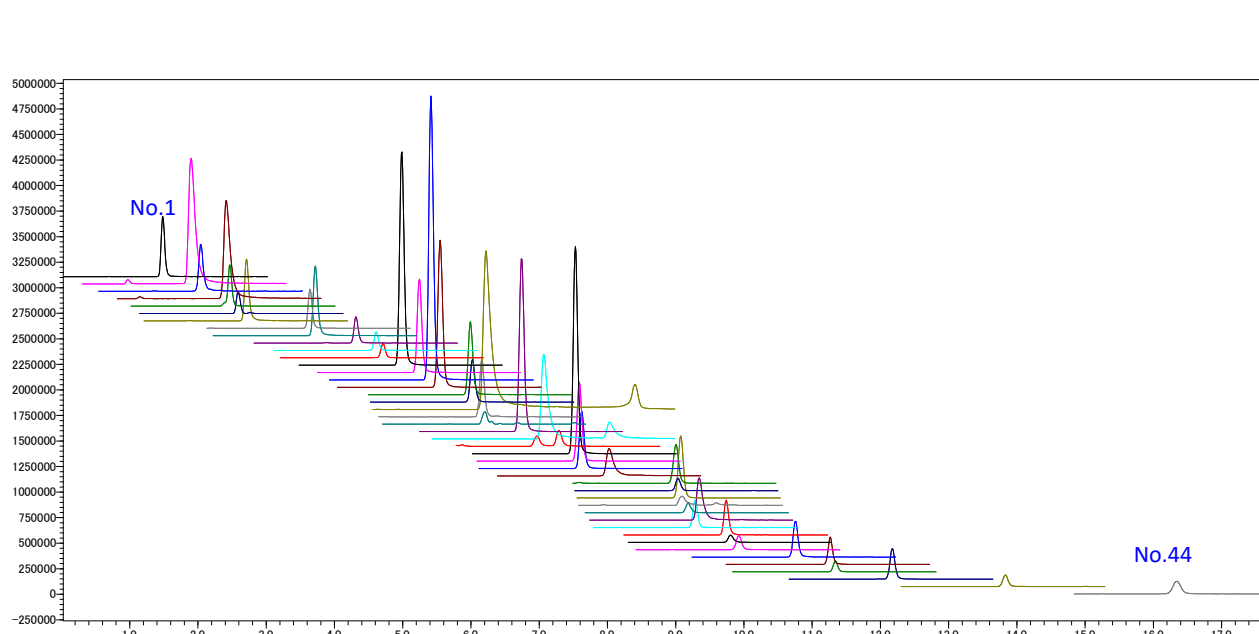


Figure 5 MRM Chromatogram of 44 azo dyes in pure solvent (20ng/mL)

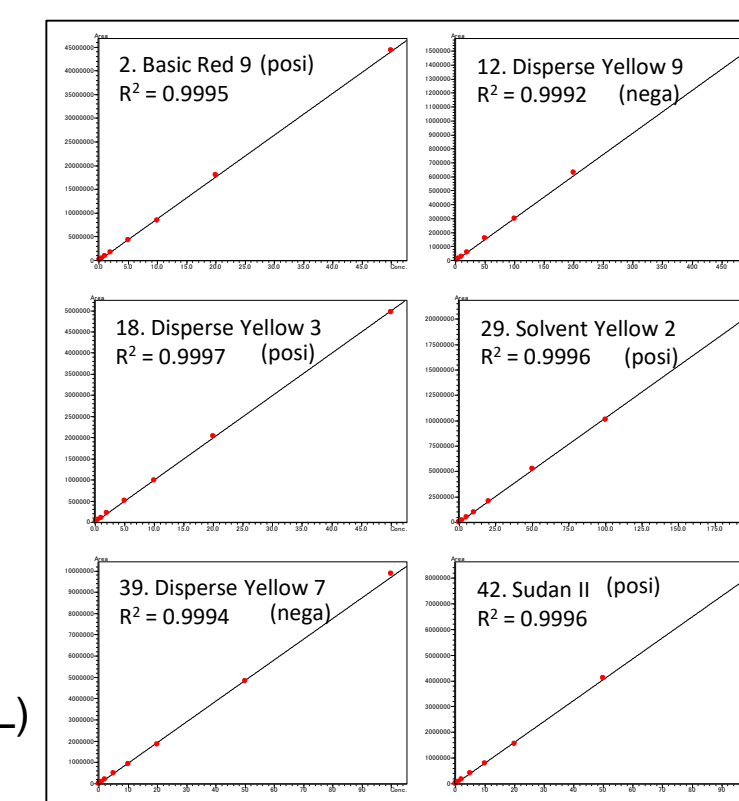


Figure 6 Calibration curves of 6 representative azo dyes

No	Compound Name	RT (min)	Linearity	Range (ng/mL)	Matrix Effect (%)	No	Compound Name	RT (min)	Linearity	Range (ng/mL)	Matrix Effect (%)		
1	Acid orange 7	1.52	0.9976	0.1-200	156.8	108.7	23	Basic violet 1	7.03	0.9940	0.5-50	108.3	71.1
2	Basic Red 9	1.90	0.9995	0.1-50	91.5	78.7	24	Disperse Blue 35	7.29	0.9981	5-500	82.8	78.6
3	Disperse Blue 1	2.05	0.9984	2-200	75.2	92.6	25	Disperse Yellow 49	7.53	0.9988	0.1-50	77.4	82.9
4	Basic Violet 14	2.42	0.9994	0.1-50	90.7	72.1	26	Solvent Yellow 3	7.59	0.9995	0.1-20	100.8	93.8
5	Acid yellow 36	2.50	0.9984	0.1-50	136.0	104.3	27	Disperse Blue 124	7.63	0.9992	0.1-20	89.0	87.8
6	Acid violet 49	2.63	0.9961	1-200	100.5	96.6	28	Basic Violet 3	8.00	0.9980	2-500	124.5	68.3
7	Disperse Blue 7	2.73	0.9967	0.1-20	89.1	90.8	29	Solvent yellow 2	9.01	0.9996	0.1-200	89.3	81.7
8	Disperse Blue 3	3.66	0.9991	0.1-20	97.0	96.8	30	Disperse Orange 37/76	9.06	0.9994	0.2-20	58.7	80.4
9	Disperse Red 11	3.72	0.9990	0.1-20	86.7	90.0	31	Michler Base	9.08	0.9991	0.2-100	99.1	85.3
10	Disperse Blue 102	4.33	0.9985	0.5-200	99.8	97.5	32	Disperse Blue 26	9.11	0.9997	0.5-50	115.8	95.2
11	Disperse Yellow 3	4.63	0.9989	0.2-50	81.8	90.1	33	Disperse yellow 56-methyl	9.19	0.9986	1-500	77.6	78.4
12	Disperse yellow 9	4.71	0.9992	2-500	43.1	82.6	34	Basic Blue 26	9.30	0.9981	5-500	121.3	53.8
13	Disperse Red 17	4.99	0.9995	0.1-20	95.8	93.9	35	Disperse orange 61	9.30	0.9986	1.0-50	58.5	78.6
14	Disperse yellow 39	5.25	0.9951	0.2-100	82.0	90.0	36	Disperse Orange 1	9.75	0.9994	0.1-50	41.9	72.8
15	Disperse Blue 106	5.43	0.9996	0.1-20	71.4	92.4	37	Disperse Yellow 23	9.82	0.9998	0.5-100	49.1	74.3
16	Solvent yellow 1	5.56	0.9995	0.1-20	88.2	91.8	38	Sudan I	9.93	0.9984	0.5-500	58.4	74.5
17	Disperse Orange 3	6.00	0.9978	0.2-20	36.4	86.7	39	Disperse yellow 7	10.76	0.9994	0.1-100	168.7	103.9
18	Disperse Yellow 3	6.03	0.9997	0.1-50	52.1	83.1	40	Disperse red 151	11.27	0.9990	5-200	59.3	75.9
19	Basic Green 4	6.20	0.9957	0.5-200	69.2	66.5	41	Disperse Orange 149	11.36	0.9983	0.1-5	89.9	97.9
20	Disperse Brown 1	6.17	0.9982	0.5-20	47.1	86.7	42	Sudan II	12.18	0.9996	0.1-100	51.7	73.4
21	Disperse Orange 11	6.19	0.9960	5-200	94.7	102.5	43	Sudan III	13.85	0.9969	5-200	91.6	83.5
22	Disperse Red 1	6.76	0.9993	0.1-20	33.1	90.1	44	Sudan IV	16.35	0.9981	5-200	52.0	76.0

3-3: Azo dyes-Method 2

The results of these analyses with LCMS-8045 provided good linearities ($R^2 > 0.99$) and wide dynamic ranges (See Table 6). Using the method developed for the method package, detection limit for the 7 azo dyes are way below the regulation values of 50mg/kg (50ppm). Similar to azo dye method 1, azo dyes showed matrix effect at range 84.3% ~ 100.8%, except for direct red 28, direct black 38 and direct brown 95 within a range of 21.8% ~ 52.3%. With dilution, the matrix effect for the three dyes could be improved to 33.5% ~ 86.1%. Thus, suggesting the effectiveness of dilution.

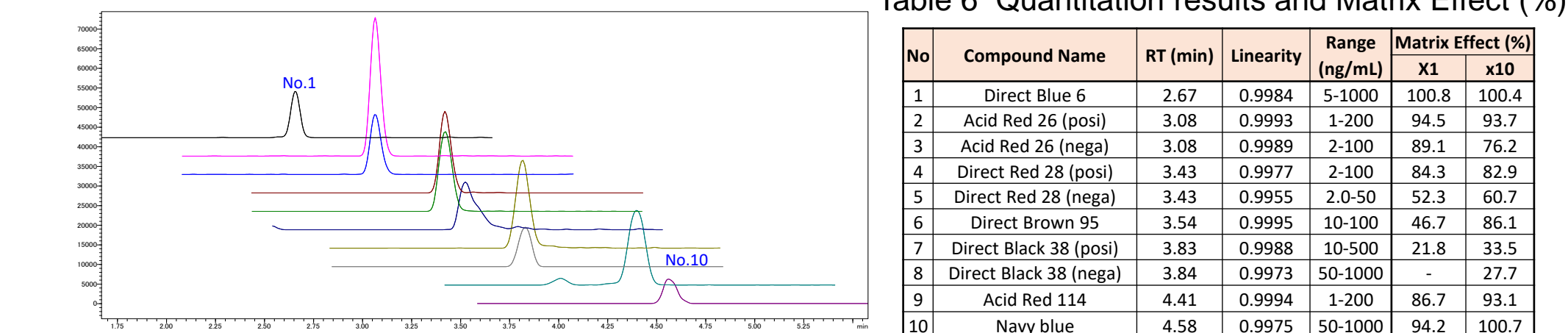


Figure 7 MRM Chromatogram (50ng/mL)

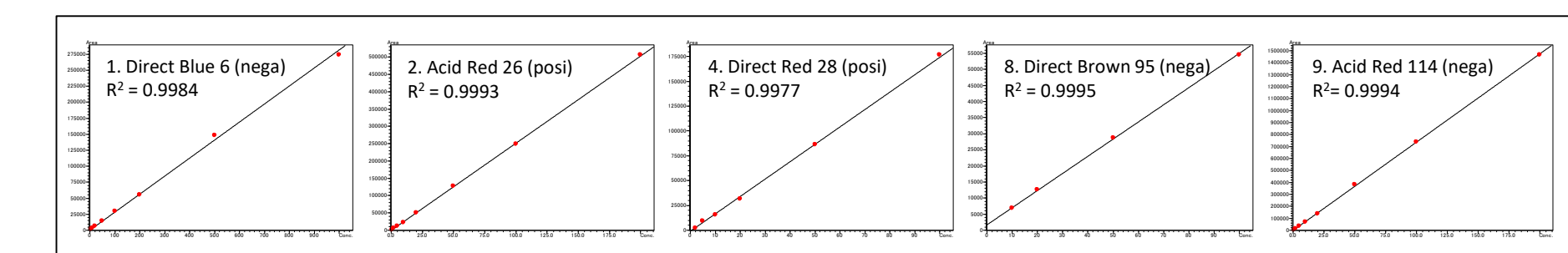


Figure 8 Calibration curves of 5 representative azo dyes

4. Conclusions

- For aromatic amines, the sample is recommended to be diluted with water due to retention. Here, we propose the co-injection method using pretreatment program with the autosampler (SIL-30AC). It can reduce human error and maximize efficiency.
- For azo dye analysis, one key issue notice is in the matrix effect test. Matrix effects can be reduced by dilution with the sample solution. Furthermore, the detection limit of the method developed is way below the regulation limit. Thus, these samples can be diluted further while ensuring detection is still within the regulation limit.
- We have developed several LC/MS/MS methods for the restricted chemicals in textiles. As shown in Figure 9, introducing a column switching system enables the analysis of all the components targeted, just by changing the combination of the mobile phase and column.

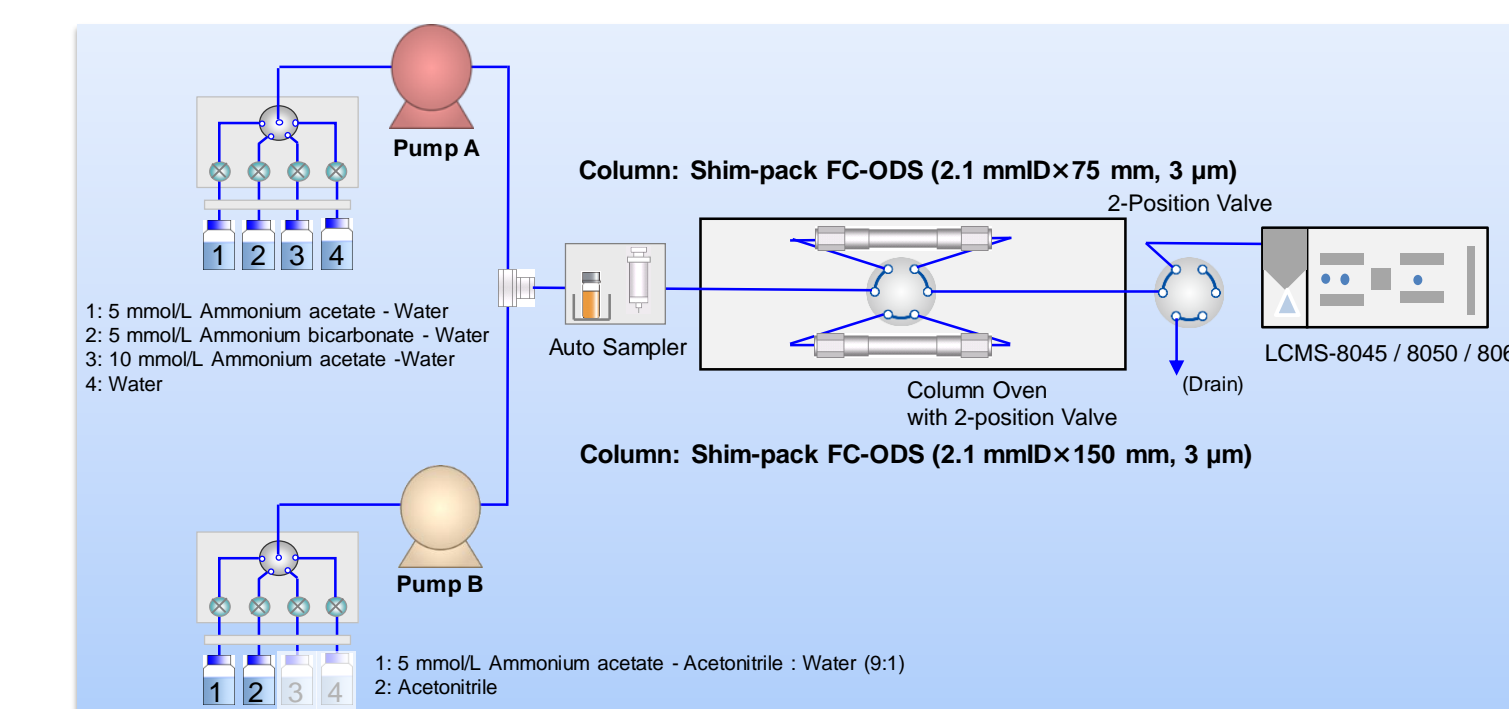


Figure 9 System Configurations (example)

5. References

- Yin Ling Chew, Jie Xing, Leonard Guan Seng Lim, Zhaoqi Zhan, ASMS 2016 poster – TP375
- Yin Ling Chew, Jie Xing, Felicia Xue Qi Tan, Yi Hao Wee, Jarren Ling Yao Tuang, Djonan Kesuma, Zhaoqi Zhan, ASMS 2017 poster – TP727

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